Surface-induced Dissociation in Tandem Quadrupole Mass Spectrometers: A Comparison of Three Designs

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Three different devices that can be used for surface-induced dissociation (SID) in tandem quadrupole instruments are compared here. The designs were compared by examining the fragmentation of several compounds including benzene, $W(CO)_6$, and $(CH_3)_4N^+$. These studies show that SID can be readily implemented on a variety of tandem quadrupole instruments and that the spectra obtained with the in-line and 90° instruments are similar. Evidence is presented that confirms that high average internal energies and narrow distributions of internal energy are available by this technique. Efficiencies for fragmentation of odd-electron ions are on the order of those previously reported by others. The overall SID efficiency for even-electron ions is higher than that for odd-electron ions of similar structure. *(J Am Soc Mass Spectrom 1992, 3, 27–32)*

Most current applications of tandem mass spectrometry involve collisions of the mass-selected ions with an inert gas such as He, Ar, or Xe [1]. Recently, Cooks and co-workers [2–4] and others [5–8] have illustrated a variety of interesting processes that occur upon low energy (eV) collisions of mass-selected polyatomic ions with a *surface*. These include (1) surface-induced dissociation (SID), in which fragmentation is promoted by conversion of some of the kinetic energy of the projectile into internal energy, (2) reactive collisions of projectile ions with surface adsorbates, and (3) chemical sputtering,[1] in which the impingement of the projectile ion at the surface causes ejection of secondary ions [2–4]. These processes and others are described in more detail in a recent review [3]. Although significant progress has been made in understanding polyatomic ion/surface collisions, this technique is still considered to be a curiosity and is not widely used as an activation method for tandem mass spectrometry experiments. We compare here three different devices that can be used for SID in tandem quadrupole instruments. Evidence is presented that confirms that high average internal energies and narrow distributions of internal energy are available by this technique.

Instrument Design

We report here results that were obtained by using three different experimental arrangements that allow collision of mass-selected ions with a surface (Figure 1). Two of the designs are in-line devices that involve simple modifications to a commercial triple quadrupole instrument, whereas the third design involves a dual quadrupole instrument built specifically for investigation of ion/surface collisions. Device 1 (slant-plate), which consists of a simple deflector plate and surface [8], was mounted in the triple quadrupole mass spectrometer (Finnigan-MAT TSQ 70, San Jose, CA). In this case, quadrupole 2 (the bent collision cell) was removed from the instrument, the SID device was mounted on the optical rail, and quadrupole 3 was moved forward and placed collinear with the first quadrupole. Device 2 (cone-cylinder) is similar to a device described by Bier et al. [9]. The cone (stainless steel, machined with a 0.14-in diameter at the base, a tip-to-base distance of 0.14 in, and a 0.025-in diameter tail extending 0.10 in from the base) is suspended by a wire from its tip and is aligned concentrically with the surrounding surface (a 0.38-in diameter stainless steel

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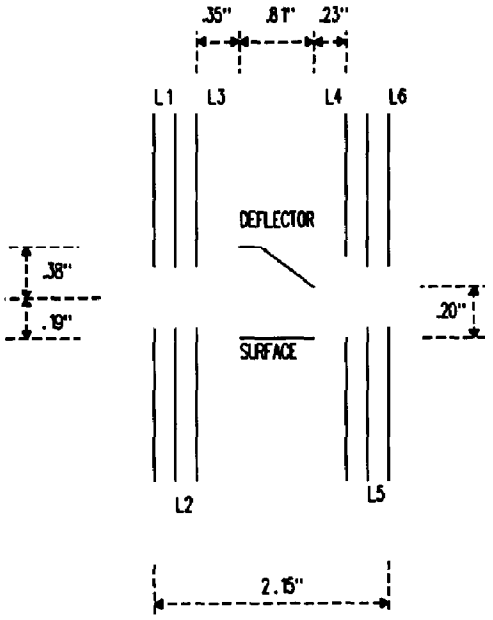
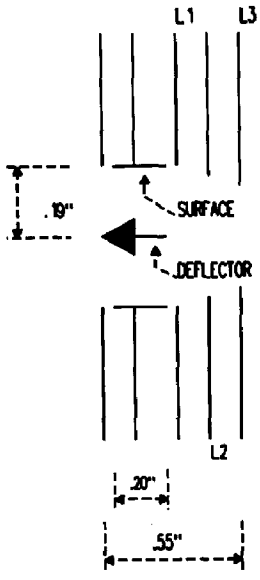
[1] Although chemical sputtering is related to secondary ion mass spectrometry (SIMS), it differs from SIMS in several respects (see ref 3): (1) low-energy (eV) projectile ions are used, (2) the extent of dissociation of the secondary ions increases with increasing collision energy, (3) it is dependent on the type of projectile ion, and (4) high secondary ion yields are detected.

1044-0305/92/$3.50

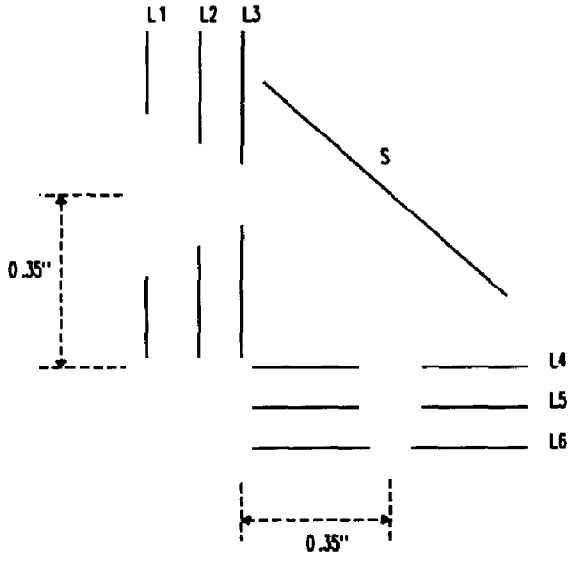
Received November 30, 1990
Revised June 18, 1991
Accepted June 20, 1991



a DEVICE 1
SLANT-PLATE



b DEVICE 2
CONE-CYLINDER



c DEVICE 3
90 DEGREE QUADS

Figure 1. Three different experimental arrangements that allow collision of mass-selected ions with a surface (see text). Further details may be obtained from the authors.

Figure 1. (*continued*).

cylinder). In our experiments, the cone-cylinder device is mounted between quadrupole 1 (mass analyzer) and quadrupole 2 (collision cell) of the triple quadrupole instrument. In previous work [9], the device was inserted between quadrupoles 2 and 3. Device 3 (Virginia Commonwealth University instrument) consists of two Extrel 4000-u quadrupole mass analyzers placed at 90° to each other with a surface placed to intersect the ion optical path of the two quadrupoles (Extrel Corporation, Pittsburgh, PA). The cone-cylinder device described above was also inserted in-line between the quadrupole mass analyzers of this instrument to allow comparison of the 90° and in-line configurations on a single instrument. Unless otherwise noted, the phrases "cone-cylinder" and "device 2" refer to the modified triple quadrupole instrument and not to the Virginia Commonwealth University instrument.

The surface used in each design was stainless steel. All experiments were performed under the normal vacuum conditions of our quadrupole mass spectrometers (10^{-7} torr) such that surface adsorbates were present (e.g., hydrocarbon background from pump oils). The ion gauge was located in the differentially pumped chamber containing the surface.

Results

Comparison of the three designs was made by using benzene and $W(CO)_6$. The benzene radical ion (m/z 78) was chosen for analysis because ion/surface colli-

sions of this ion result in characteristic dissociation products, as well as ions thought to result from H and CH_3 abstraction from surface adsorbates [10, 11].[2] The $W(CO)_6$ ion was investigated because its simple fragmentation pattern of consecutive CO losses and known dissociation energetics allow estimation of the amount of internal energy deposited by a given activation method [12].[3] Additional data for several other compounds were also obtained for the cone-cylinder and 90° designs and are described briefly below.

Figure 2 compares the spectra that result when the benzene molecular ion (m/z 78; $[C_6H_6]^{+\cdot}$) is mass-selected and allowed to collide with a surface at 30 eV using devices 2 and 3, respectively (the spectrum for device 1 is similar). Benzene spectra obtained on the three devices at various collision energies (10-80 eV) are quite similar, and they are also similar to those previously published by Hayward et al. [10]. The results show that the amount of internal energy deposited at any given collision energy is relatively insensitive to the instrumental configurations used here. For example, the variation of ion abundance ratios (such as $[C_6H_5]^+/[C_6H_6]^{+\cdot}$ and $[C_4H_3]^+/[C_4H_4]^{+\cdot}$) with collision energy is similar for all three devices. A possible explanation for this similarity is that the angles of ion incidence and extraction at the surface are approximately the same for the three devices, despite the overall differences in configurations. This is supported by calculated ion optical trajectories (determined by the SIMION[4] program) that suggest that ions strike and leave the surface at roughly 45° angles even in the in-line devices.

Previous studies have shown that a relatively narrow distribution of internal energy is deposited into a projectile ion upon collision with a surface and that the position of this distribution can be varied by changing the collision energy [3, 13]. Our results with benzene are in agreement with this, as are the following results for $W(CO)_6^+$ and $(CH_3)_4N^+$. Figure 3 shows a comparison of relative daughter ion abundances of $W(CO)_6^{+\cdot}$ as a function of collision energy (1) for SID, (2) for collision-induced dissociation (CID) in a triple-quadrupole mass spectrometer (single-collision conditions, Ar target), and (3) for CID at 8 keV (He target). (The SID results are shown for devices 1 and 3; the results for device 2, although omitted here, are nearly

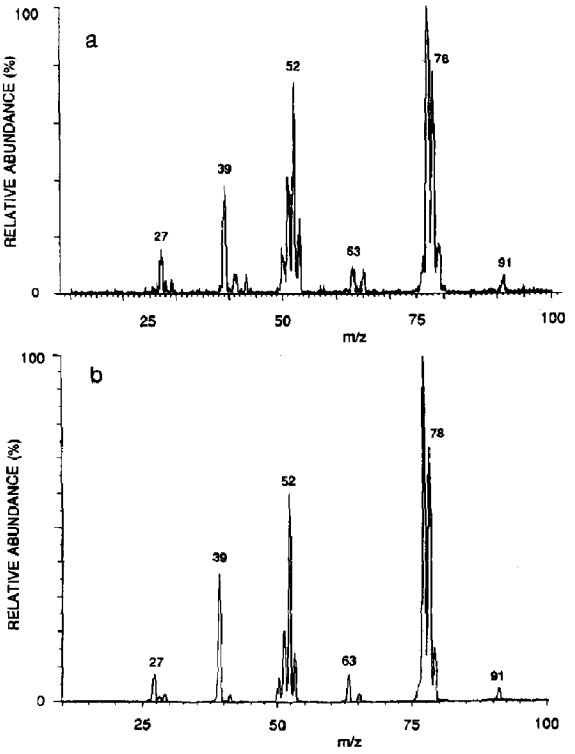


Figure 2. Spectra that result when ionized benzene (m/z 78) is mass-selected and allowed to collide with the surface at 30 eV. (a) Device 2 [inserted between Q1 and Q3 of the TSQ70] and (b) device 3. The signal-to-noise ratio obtained by using device 2 (a) was substantially improved (spectrum not shown) when device 2 was inserted into the QQ instrument at Virginia Commonwealth University, but was still not equal to that obtained for the 90° arrangement (device 3) at Virginia Commonwealth University.

identical to those for device 1.) A given daughter ion appears over a relatively narrow range of laboratory collision energies in the SID spectra. For example, $W(CO)_4^+$ dominates the SID spectrum at a lab collision energy of 30 eV while $W(CO)_3^+$ dominates at 40 eV. The product distribution widths observed for in-line SID are somewhat broader than those observed for the 90° instrument. This difference may result from a wider range of angular trajectories for the in-line devices. Nevertheless, all three SID experiments result in the deposition of narrow distributions of internal energies. This is in clear contrast to CID experiments that indicate deposition of a much broader distribution of internal energies [12]. The CID spectra of Figure 3 show that fragment ions with internal energy requirements [12] for fragmentation ranging from 1.2 to 17.4 eV are detected at a single laboratory collision energy. However, the fragment ion with the lowest energy requirement ($W(CO)_5^+$) dominates the spectra obtained by both low (10-200

[2] The ion at m/z 91 ion is thought to be the result of methyl abstraction from surface adsorbates followed by loss of H_2 (see refs 3, 4, 10, and 11). The ion at m/z 65 is a fragmentation product of m/z 91. Additional reaction products have been detected (e.g., m/z 103, 105, 115, 128) and will be discussed in more detail in a future publication.

[3] The consecutive CO losses from $W(CO)_6$ have similar entropy requirements and known critical energies. The relative abundance of each fragment ion, divided by the energy range over which it occurs, gives a single probability value that corresponds to the average energy in this interval. For further details, see refs 3, 12, and 13.

[4] Idaho National Engineering Laboratory, EG & G Idaho Inc., P.O. Box 1625, Idaho Falls, ID 83415.

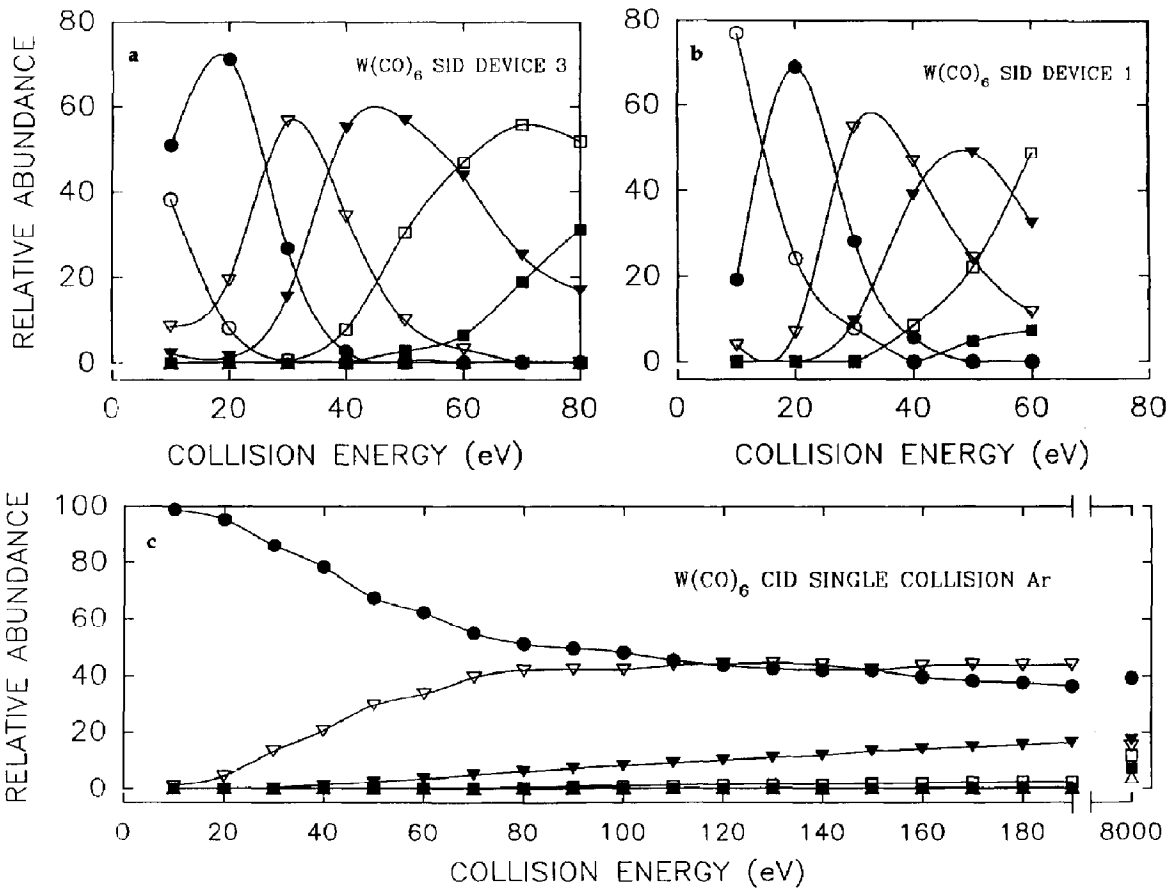


Figure 3. Energy-resolved tandem mass spectra of $W(CO)_6$ obtained by using (a) SID device 3, (b) SID device 1, (c) CID with Ar at 10–200 eV (single-collision conditions) and CID with He at 8000 eV. (○) $W(CO)_6^{+\cdot}$; (●) $W(CO)_5^{+\cdot}$; (▽) $W(CO)_4^{+\cdot}$; (▼) $W(CO)_3^{+\cdot}$; (□) $W(CO)_2^{+\cdot}$; (■) $W(CO)^{+\cdot}$.

eV) and high energy (8 keV) CID. Based on the known thermodynamics of fragmentation of the $W(CO)_6$ ion, the amount of the lab frame energy converted to internal energy can be estimated.[3] The results of these estimates are shown in Figure 4 for the three SID devices. This figure shows that the average increase in internal energy is roughly linear with the laboratory collision energy and ~ 13% of the laboratory collision energy is converted into internal energy.

Additional evidence for the deposition of a narrow distribution of internal energies upon collisions of polyatomic ions with a surface is presented in Figure 5. This figure shows the energy-resolved spectra that result when the tetramethylammonium ion, $(CH_3)_4N^+$, is mass-selected and allowed to collide with the surface in devices 2 and 3. The calculated breakdown curve [1b] indicates that this ion fragments at low energies by loss of CH_4 via a rearrangement, at higher energies by direct loss of CH_3, and at even higher energies by loss of CH_3 followed by loss of H (an apparent loss of CH_4). The agreement between the calculated breakdown curve (plot of relative ion abundances versus internal energy) and the SID data is consistent with the deposition of a narrow, "tunable" distribution of internal energies. The maximum energy deposition is varied or "tuned" by changing the collision energy. A simple broadening of the internal energy distribution with increasing internal energy would not lead to the results observed.

Efficiency

A key consideration of the potential analytical utility of polyatomic ion/surface collisions is the sensitivity of the technique. Cooks et al. [3] have reported that ~ 1–14% of the parent ions directed onto the surface are recovered as fragment ions or unfragmented parent ions. Although these types of measurements are dependent on several instrumental and experimental factors, we have attempted to characterize the SID efficiencies for the instruments in this study. For the in-line experiments, characterization of the ion transmission through the device without surface collisions

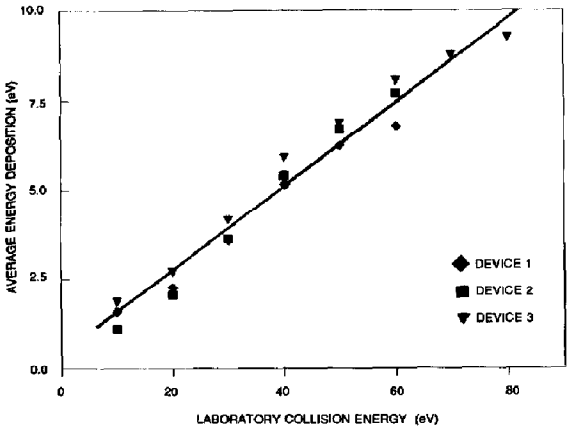


Figure 4. The average internal energy of $W(CO)_6$ after collisions with a stainless-steel surface. The diamonds correspond to data taken with device 1, the squares correspond to data taken with device 2, and the upside-down triangles correspond to data taken with device 3. On average, 13% of the kinetic energy of the projectile ions is converted into internal energy.

is complicated by the absence of a line of sight through the device. Nevertheless, it is possible to set up instrumental conditions such that most ions are transmitted without striking either the deflector or the surface (as suggested by ion current measurements made at both sites). In the 90° instrument, ions can be easily transmitted without striking a surface although some signal loss may result from nonaxial ion trajectories in the second quadrupole (a result of curving the ions past the surface). In both types of instruments, transmission was measured by adjusting voltages to maximize ion throughout. Conditions were then adjusted to maximize SID yield at a given collision energy. For transmission and SID measurements, both quadrupoles were set for mass analysis (not radiofrequency-only) and good peak shape and resolution were maintained.

For all devices, the SID yield varied as a function of collision energy and the structure of the parent ion. The results are summarized in Table 1 for the cone-cylinder and 90° devices. Data are not included for the slant-plate device because efficiencies for this device were found to be very low (e.g., 0.05% for benzene). As a result, further studies with this device have not been pursued. The low efficiencies for the slant-plate device may be attributable to the difficulty in collecting ions after they strike the surface; voltages sufficient to draw ions off the surface tend to distort the trajectories needed to focus ions on the surface. Additionally, the slant-plate device does not efficiently utilize the axial symmetry of the ion optical flight path.

The results for the cone-cylinder and 90° devices suggest that the efficiencies are higher for the 90° device. It is difficult to assess the origin of this difference. One possibility is that the transmission measurement is biased in the 90° device relative to the cone-cylinder device (e.g., if the transmission measurement for the 90° device is low, the apparent efficiency is high). A second factor may be differences in the behavior of the quadrupoles used to collect the fragment ions (instruments made by two manufacturers are being used). Evidence for this explanation is found in efficiency measurements made when the cone-cylinder device was installed on the Extrel instrument at Virginia Commonwealth University (after

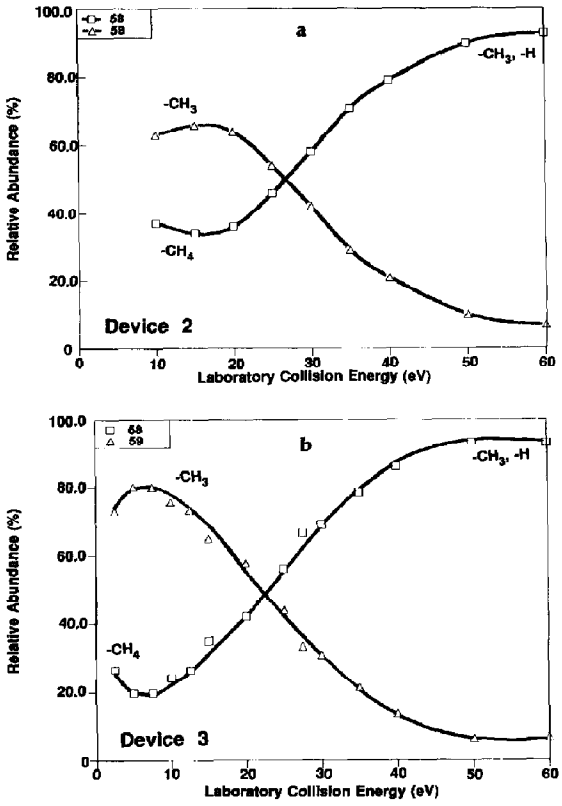


Figure 5. The influence of the SID collision energy on the relative abundances of the fragment ions of m/z 59 and m/z 58 from mass-selected $(CH_3)_4N^+$. (a) Cone-cylinder device. (b) 90° device.

Table 1. SID Efficiencies

	30 eV SID	
Parent Ion	Device 2 (Cone-cylinder), %	Device 3 (90° quads), %
Benzene $M^{+\cdot}$	0.2	1
Benzene $[M + H]^+$	0.8	7
Pyridine $M^{+\cdot}$	0.6	2
Pyridine $[M + H]^+$	5	19
$(CH_3)_4N^+$	3	8
$(CH_3CH_2)_4N^+$	7	10

placing the quadrupoles in an in-line configuration). This arrangement yielded an efficiency for benzene approximately equal to that obtained for the 90° arrangement (higher than the value obtained for the cone-cylinder device on the triple-quadrupole instrument). A third possibility is that the cone-cylinder device suffers from poor fragment collection optics (i.e., there are interferences between focusing the ions on the surface and extraction of the ions from the surface). The inability to focus and collect ions at energies above 70 eV with device 2 tends to support the latter point. Because instruments of significantly different configuration are being compared, it is difficult to state definitively whether the efficiencies for 90° devices will be uniformly higher than those for in-line devices. However, our experience with the two configurations suggests that it is easier to tune the 90° configuration, and the signal-to-noise ratios obtained under roughly similar ion source conditions are higher on the 90° device.

Another factor that plays a role in SID efficiency is the structure of the ion. Our recent studies in both the 90° and in-line configurations have been extended to even-electron ions formed by fast atom bombardment or chemical ionization. There are significant differences between the efficiencies for odd- and even-electron ions of similar structure and mass (Table 1). For a given device, the protonated counterpart of the odd-electron ion gave the higher efficiency. Data have been obtained on the cone-cylinder device for acetone (0.4%) and protonated acetone (0.8%) that are consistent with this trend. Additionally, quaternary ammonium ions tend to give higher efficiencies than the odd-electron ions examined. This may result from the relatively low electron affinities of protonated and quaternary ammonium ions relative to odd-electron ions. The corresponding lower propensity for neutralization allows more fragments to survive as ions. This result is important because many current applications of tandem mass spectrometry require fragmentation of large, even-electron ions.

Detection limit measurements were not a goal of this research and are complicated by many factors including the SID efficiency, the ion source type, the detector used, etc. However, we have been able to obtain SID spectra of peptides on the 90° device at the 100–200 pmol level (total sample introduced on probe tip) with excellent signal-to-noise ratios. By extrapolation, we expect optimized detection limits on the order of 10–20 pmol.

Summary

These studies show that SID can be readily implemented on a variety of tandem quadrupole instruments. The spectra obtained with the in-line and 90° instruments are similar. Efficiencies for fragmentation of odd-electron ions are on the order of those previously reported by Cooks et al. [3]. Our work demonstrates striking similarities in energy deposition that are relatively instrument-independent. The percentage of the collision energy that is converted to internal energy is in agreement for the three different configurations and agrees with previously reported results [3]. The overall SID efficiency for even-electron ions is higher than that for odd-electron ions of similar structure. The yields of fragment ions compared to the transmitted parent ion are comparable to, or higher than, those observed for low-energy CID under single-collision conditions or for high energy CID. In terms of overall sensitivity and control of energy deposition, the 90° configuration is preferable to the in-line devices examined. However, the cone-cylinder in-line device gives reasonable results and can be easily inserted into an existing tandem mass spectrometer.

Acknowledgments

The work performed at Virginia Commonwealth University was funded by the Office of Naval Research, the Society for Analytical Chemists of Pittsburgh, and the Thomas F. and Kate Miller Jeffress Memorial Trust. FLK gratefully acknowledges support from the NRC and the NRL in the form of a NRC/NRL Cooperative Research Associateship.

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